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A Fundamental Approach to Developing Aluminium-based Bulk Amorphous Alloys based on Stable Liquid-Metal Structures and Electronic Equilibrium - 154041

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14. ABSTRACT
The primary aim of this research project was to apply a novel topological and electronic-based model recently developed by the principal investigator in collaboration with the US Air Force Research Laboratory for accurately predicting compositions of new amorphous alloys specifically based on aluminium with properties superior to commercial crystalline metals and existing amorphous alloys. This research investigated alloy families that contained a variety of elements including Al, Cu, Ni, Zr, Mg, Pd, Ga, Ca. Many new Al-based amorphous alloys were found within the numerous alloy systems studied in this project, and these were found specifically in compositional regions predicted by our amorphous alloy structural model. However, the critical casting dimensions of these alloys were still considered as sub-millimetre, and hence could not producible as bulk specimens of substantial size for practical structural applications. To date, the crystallisation kinetics of these Al-based alloys is difficult to supress by cooling rates achievable by standard casting practices. Some systems remain good candidates for further studies which will be pursued beyond the length of this project.

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"A Fundamental Approach to Developing Aluminium-based Bulk Amorphous Alloys based on Stable Liquid-Metal Structures and Electronic Equilibrium"

Date: 16/03/2017

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ABSTRACT

Many new Al-based amorphous alloys were found within the numerous alloy systems studied in this project, and these were found specifically in compositional regions predicted by our amorphous alloy structural model. However, the critical casting dimensions of these alloys were still considered as sub-millimetre, and hence could not producible as 'bulk' specimens of substantial size for practical structural applications. To date, the crystallisation kinetics of these Al-based alloys is difficult to supress by cooling rates achievable by standard casting practices. Some systems remain good candidates for further studies which will be pursued beyond the length of this AOARD funded project.

INTRODUCTION: Amorphous alloys or bulk metallic glasses (BMGs) are a relatively new class of materials that exhibit a disordered amorphous (glassy) atomic structure as opposed to an ordered crystalline structure found in regular alloys.[1] These exciting new materials have received considerable attention recently in both fundamental science and in industry due to their remarkable and unique suite of properties including exceptionally high specific strengths and hardness (2-3 times stronger than their crystalline counterparts), an elastic limit twice that of a crystalline metal, corrosion and wear resistance and low mechanical dampening.[1,2] Furthermore, being glassy these alloys display glass transition phenomenon, whereby above the glass transition temperature they may be formed like plastics or regular ceramic glasses, hence these materials can be produced in shapes simply unachievable by regular crystalline metals, opening up a window of new and previously un-thought applications for metals.[2]

Aluminium and its alloys are one of the most largely produced and recycled metals (second only to iron/steel). It is low cost, exceptionally light-weight and corrosion resistant. Despite BMGs of relatively large dimensions (inches) being produced in magnesium, copper, nickel, zirconium and rare-earth based alloy systems over the past 2 decades, no large BMGs have been reported in aluminium-based alloy systems.[3] The formation of an aluminium-based BMG, by metallurgists and physicist alike, is considered the 'holy grail' within this field.

Fundamentally, the crystallisation of an alloy melt is a diffusion-based process, driven by thermodynamics and kinetics. In a thermodynamic sense, particular elements may be alloyed in specific concentrations such that the crystallization of high melting point intermetallics is avoided and mixing is promoted. On the other hand, the ability to slow crystallization kinetics when cooling from the molten state may be achieved topologically by having dense atomic packing configurations within the liquid structure which jams or severely hinders atomic movement/diffusion.[4]

Recently, the applicant and US Air Force collaborator Dr Daniel Miracle have developed a new predictive model[4,5] based on the geometric packing of atoms and the structures observed in BMGs (the building blocks of a glass). This model identifies the specific radius ratios of atoms in multicomponent systems and their exact concentrations to achieve efficient (tight) packing of all atoms within the amorphous structure. Further it is then possible to select specific cluster structures that frequently show difficulty in translating from a liquid to a regular crystal structure (symmetry based). The applicant has also shown that a strong correlation exists between the compositional occurrence of eutectic reactions, specific efficiently-packed atomic clusters with preferred coordination numbers and symmetry,[6-9] free electrons per cluster and stable electronic shell closings in accordance with the nuclear convention (unpublished works). This is thought to relate closely to the recent 'superatom' theory, which has clearly demonstrated the relationship between cluster stability in pure metals and atomic shell closings, which will also be utilised and explored further in this work.[10]

By satisfying the aforementioned ***thermodynamic***, ***kinetic*** and ***electronic*** conditions, new and improved high glass-forming alloy compositions may be predicted, providing a specific, novel and innovative approach for producing aluminium-based BMGs or other new glass-forming systems.

AIMS: The primary aim of this research project is to apply a novel topological and electronic-based model recently developed by the applicant in collaboration with the US Air Force (Dr Daniel B Miracle) for accurately predicting compositions of new amorphous alloys specifically based on aluminium with properties superior to commercial crystalline metals and existing amorphous

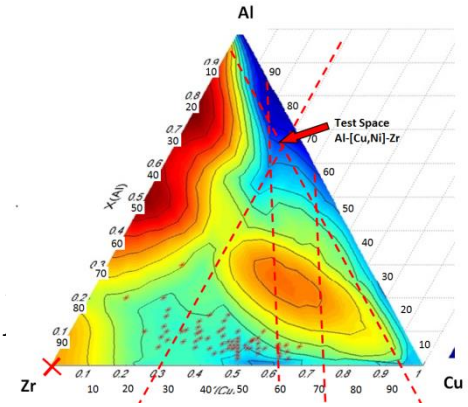
EXPERIMENTAL METHODS: Recently, Laws and US Air Force collaborator Dr Daniel Miracle have developed a new predictive model based on the geometric packing of atoms and the structures observed in BMGs (the building blocks of a glass). This model identifies the specific radius ratios of atoms in multicomponent systems and their exact concentrations to achieve efficient (tight) packing of all atoms within the amorphous structure. Further it is then possible to select specific cluster structures that frequently show difficulty in translating from a liquid to a regular crystal structure (symmetry based). Several potential alloy systems and specific composition spaces have been identified by Laws for the formation of an aluminium-based bulk glass. Specifically these include select compositions from the Al-Cu-Ni-Zr, Al-Cu-Ni-Mg, Al-Pd-Mg and Al-Mg-Ga-Ca alloy families, focussing on compositions with an aluminium content of at least 75 atomic percent. The inclusion of elements such as magnesium and calcium also assists in maintaining an exceptionally low density of the proposed alloys.

Alloys are melted in either a vacuum arc furnace or induction furnace in an inert argon atmosphere and cast into wedge-shaped copper moulds to give a linear variation in sample cooling rate. The resulting casting gives the indication of the alloys propensity to form a glass and the required cooling rate for glass formation. At least 2 samples of each composition were fabricated.

As-cast samples then undergo a series of standard characterisation tests to confirm their amorphous nature including X-ray diffraction, standard optical and scanning electron microscopy to identify any crystallites that may be present. Further, differential scanning calorimetry analysis was carried out on appropriate samples to determine the thermophysical properties of these alloys e.g. glass transition temperature, crystallisation temperature and melting/liquidus temperatures. No samples were deemed 'large enough' to perform mechanical testing.

Al-Cu-Ni-Zr & Al-Ni-Co-Zr Systems

The Al-Cu-Zr, Al-Ni-Zr & Al-Co-Zr systems are known to exhibit high glass-forming ability in the Zr-[Cu,Ni,Co] rich region. A range of Al-Cu-Ni-(Co)-Zr alloys were tested for glass-forming ability. The maximum casting thickness achieved in this alloy family for an Al-based glass was ~400um for the $Al_{72}Cu_{19}Ni_5Zr_4$ alloy.



Composition	Critical Casting Thickness (µm)	Notes
$Al_{76}Cu_{19}Zr_5$	<50	minimal glass
$Al_{74.5}Cu_{15}Ni_5Zr_{5.5}$	200, 209	high melting temp
$Al_{74}Cu_{16}Ni_5Zr_5$	220, 234	
$Al_{73}Cu_{18}Ni_5Zr_4$	294, 299	
$Al_{72}Cu_{19}Ni_5Zr_4$	357, 397	Highest GFA in system
$Al_{70}Cu_{21}Ni_5Zr_4$	<100	GFA lost
$Al_{75.5}Ni_{19}Zr_{5.5}$	<100	high melting temp
$Al_{82}Ni_{13}Zr_5$	113, 127	
$Al_{82}Ni_{11}Zr_5Co_2$	~100	high melting temp

Comments: Zr was found to raise the melting point of these alloys very quickly, reducing the melts' ability to supercool when cast, hence better results were achieved at slightly lower Zr contents. Better results may be achieved with temperature control in an induction furnace set up, however this would still not likely produce a bulk glass. Compositional refinement of the $Al_{72}Cu_{19}Ni_5Zr_4$ composition may give a 0.5 mm glass.

Al-Cu-Ni-Mg

This alloy family is topologically identical to Al-Cu-Ni-Zr, hence compositions were chosen in similar composition space. A deep ternary eutectic reaction is also known to exist near $Al_{75}Cu_{17}Mg_8$ and a peritectic reaction at $Al_{70}Cu_{20}Mg_{10}$, making this system quite attractive. However Glasses were produced using induction melting equipment and copper mould casting with critical casting sizes up to ~350um.

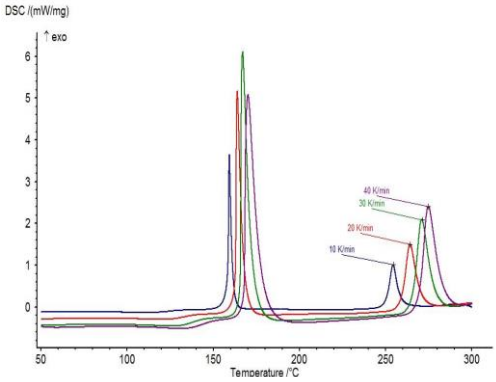


Figure 2*: DSC traces of the $Al_{71.3}Cu_{16}Ni_5Mg_{7.7}$ alloy at different heating rates revealing a prominent glass transition relaxation.*

Composition	Critical Casting Thickness (µm)	Notes
$Al_{75}Cu_{10}Ni_7Mg_{10}$	<100	v.high melting point
$Al_{73}Cu_{16}Ni_3Mg_{10}$	289, 312	low melting point
$Al_{71.3}Cu_{16}Ni_5Mg_{7.7}$	319, 327,346	high thermal stability
$Al_{70}Cu_{18}Ni_5Mg_7$	213, 240	
$Al_{67}Cu_{18}Ni_5Mg_{10}$	160, 170	
$Al_{65}Cu_{20}Ni_5Mg_{10}$	<100	

Comments: Ni addition to the Al-Cu-Mg system quickly raises the melting point of these alloys, making them difficult to process due to magnesium evaporation, however Ni is essential for glass formation – the Al-Cu-Mg ternary system does not form glasses in this region at all. Work in this system was limited and shall be pursued further for compositional optimisation.

Al-Pd-Mg System

The Al-Pd-Mg system is known to form quasi-crystals over a broad composition range which are topologically closely related to glass-forming structures. These alloys have a relatively low melting point and were prepared in an induction furnace with accurate melting and casting temperature control. Using the packing efficiency model, a compositional region was identified and a local maximum in glass forming ability of ~200um was located at a composition of $Al_{73}Mg_{13.5}Pd_{13.5}$. Microscopy results indicated the formation of pentagonal 5-fold or decagonal 10-fold quasi-crystals in the as-cast microstructure.

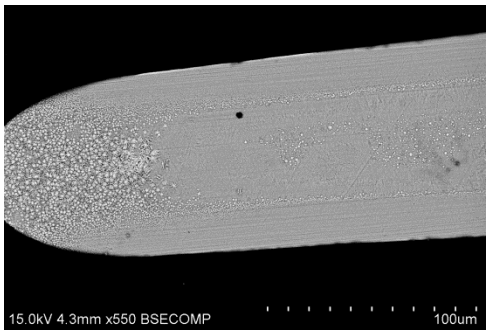


***Figure 3**: SEM micrograph showing amorphous skin and evolution of 5-fold quasicrystals in $Al_{75}Mg_{15}Pd_{10}$*

Composition	Critical Casting Thickness (µm)	Notes
$Al_{76.9}Mg_{15.4}Pd_{7.69}$	80, 96	Cast @ 700 °C
$Al_{75}Mg_{12.5}Pd_{12.5}$	130, 135	Cast @ 700 °C
$Al_{75}Mg_{15}Pd_{10}$	80, 112	Cast @ 700 °C
$Al_{73}Mg_{13.5}Pd_{13.5}$	202, 213	Cast @ 700 °C
$Al_{73}Mg_{10}Pd_{17}$	122, 143	Cast @ 750 °C
$Al_{71.4}Mg_{14.3}Pd_{14.3}$	<50	Cast @ 750 °C
$Al_{75}Mg_{9.5}Pd_{12.5}Ca_3$	<50	Cast @ 800 °C

Comments: The glass forming ability of this system was quite low, which may have been expected given that the atomic size difference between Al and Pd is quite small. It is anticipated that the addition of Ni or Cu to this system would improve this situation and the glass-forming ability of this alloy family.

Al-Mg-Ga-Ca

We had previously found high glass-forming ability in Mg-rich Mg-Al-Ga-Ca alloys in excess of 1mm in size. Based on efficient atom packing calculations, the glass forming region was expected to extend in Al-based composition space.

***Figure 3**: Optical etched micrograph showing amorphous tip of $Al_{40}Mg_{40}Ga_{15}Ca_5$ and amorphous skin of $Al_{45}Mg_{40}Ga_{10}Ca_5$*

Composition	Critical Casting Thickness (µm)	Notes
$(Mg_{70}Al_{11}Ga_{11}Ca_5Ni_3)$	1100	Mg-rich example
$Mg_{50}Al_{22.5}Ga_{22.5}Ca_5$	440	
$Al_{35}Mg_{35}Ga_{25}Ca_5$	180, 200	
$Al_{40}Mg_{40}Ga_{15}Ca_5$	220, 223,	Local GFA Maxima
$Al_{45}Mg_{35}Ga_{15}Ca_5$	~60	
$Al_{45}Mg_{40}Ga_{10}Ca_5$	~80	
$[Al_{40}Mg_{40}Ga_{15}Ca_5]Ni_1$	0	Completely Nanocrystalline

Comments: The glass forming ability of this system in the Al-based region was quite low and within a relatively narrow composition range. This work is quite preliminary and improvements could likely be made with respect compositional refinement around the $Al_{40}Mg_{40}Ga_{15}Ca_5$ composition. Possible improvements could also be made through the partial substitution of Zn which was found to be the case in the related Mg-based metallic glass work.

CONCLUDING REMARKS: This work has quickly probed the glass-forming ability of potential alloy systems indicating that whilst our theoretical model can reliable locate compositional regions of glass-forming ability, the glass-forming ability of Al-based alloy systems is considerably low. Additional compositional refinement of the alloy systems presented is likely to marginally improve glass forming ability, however given the current results; it is unexpected that these systems will produce bulk sized samples in excess of 1mm critical casting size.

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List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a) papers published in peer-reviewed journals:

None to date*

b) papers published in non-peer-reviewed journals or in conference proceedings:

None to date

c) conference presentations:

None to date

d) manuscripts submitted but not yet published:

None to date

e) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

- Dr Daniel B. Miracle, Materials & Manufacturing Directorate, Air Force Research Laboratory
- Dr (Colonel) Wynn Sanders, formerly US Air Force/AFRL.

* *It is anticipated with a little more laboratory work and compositional exploration that at least some of this work shall be published in the future, at which time AOARD and AFRL collaborators shall be included and duly acknowledged.*